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PENTOL'S EXPERIENCE TO RESTRUCTURE EMISSION MONITORING SYSTEMS IN SUCH A WAY AS TO MEET WASTE FUEL COMBUSTION REQUIREMENTS

Current regulations state the scope of Continuous Emission Monitoring Systems depending of the fuel burnt. If waste fuels are combusted three additional measurements have to be carried out continuously, i.e., the concentration of HCl, HF and total organic carbon. This paper reviews available measuring techniques required by regulations. They differ from those applied in basic measurements, therefore the retrofit of existing analysers is almost impossible (except of that for HCl determination). The results achieved are discussed. The concept of CEM systems recently implemented by PENTOL in three Polish cement plants is presented. The experience gained allows a conclusion that the systems described in the paper are characterized by the features declared.

1. INTRODUCTION

Current Polish law [1] passed in accordance with Directive 2001/80/EC (Large Combustion Plant Directive) states the scope of continuous emission monitoring (CEM), depending on the kind of the fuel burnt.

Table 1 compares the scope and reference methods of a continuous monitoring of flue gases discharged into the atmosphere in the vicinity of incinerating plants and waste fuel combustion/co-combustion plants.

The scope of continuous measurements in the case of combustion or co-combustion of waste fuels (according to Appendix 6 to the Regulation of the Minister of Environment of the 23rd December 2004 on requirements concerning the measurement of emission [1]) is more extensive in comparison to that of standard fuel combustion specified in Appendix 1.

There are three additional species to be measured:

- Hydrogen chloride (HCl).
- Hydrogen fluoride (HF).

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- Total organic carbon (TOC).

Table 1

Scope and reference methods of CEM measurements

Compound	Reference method	Basic fuels	Waste fuels
Total dust	any method verified by isokinetic sampling	+	+
SO ₂	IR absorption or acc. to ISO 7935	+	+
NO _x	IR absorption or acc. to ISO 10849	+	+
CO	IR absorption	+	+
HCl	IR absorption		+
HF	IR absorption		+
TOC	Flame Ionisation Detection (FID)		+

Most of power combustion plants obliged to measure continuously their emissions have already installed CEM systems and there is a wide choice of competitive solutions and successful suppliers. In the case of waste fuel combustion, however, the choice is not so wide and seems to be more difficult. Experience shows that measuring systems are both definitively positively and negatively reviewed. The customers should evaluate the system not only from the point of view of its performance, but they also should take account of operational and maintenance expenses.

The author's intention is not to compare and evaluate competitive solutions, but to justify the choice and to describe the solutions positively implemented by Pentol in several Polish cement plants.

2. CHOICE OF INSTRUMENTS – TECHNICAL DISCUSSION

Polish law states that the systems for monitoring a continuous emission have to be installed only in these cement plants that incinerate waste fuels. Since such an incineration seems to be a profitable business without any negative influence on the process, most of Polish cement plants either have already installed CEMs or will do it in near future.

Technical aspects of the choice and operation of instruments for measuring the concentration of HCl, HF and TOC are described below.

2.1. MEASUREMENTS OF HCl AND HF CONCENTRATION

The measurement of the concentration of HCl and HF is based on IR absorption. Choice must be made in favour of extractive or “in situ” method. Both techniques are commonly accepted and none of them is considered better. There are, however, clear reasons in favour of “in situ” method, such as:

- Low maintenance cost.

- Measurement results not disturbed by partial dilution of measured species in condensate extracted from the sample.
- Live water vapour measurement available.

Since the latest solutions of “in situ” instruments enable on-line zero calibration and span verification, the application of “in situ” method is almost unlimited, particularly in power and cement industries. Common practise confirms that, particularly in the case of cement industry applications, “in situ” analysers are most suitable.

As far as retrofit of existing CEMs is concerned it is almost not possible to add HCl and HF measuring channels to existing extraction instruments. Adding “in situ” instruments seems to be the optimum solution. Two options are considered:

- 1. “In situ” multigas analyser with HCl measurement channel.

The instruments of such a type operate in UV or IR bands; however, all gases whose concentration ought to be monitored, i.e., SO₂, NO_x, CO, CO₂, water vapour and HCl, if necessary, can be simultaneously measured in medium IR band only, using non-dispersive infrared (NDIR) technique. It is, however, necessary to take account of the fact that some of the species of interest are often “masked” by the presence of the major products of combustion such as CO₂ and H₂O. In other cases, the sensitive wavelengths of the species of interest are very close to the sensitive wavelengths of another species, hence an attempt to isolate the effects of these species using conventional infrared or ultraviolet spectroscopy is fruitless. Under these circumstances it is necessary to use the principle of Gas Filter Correlation (GFX) for accurate analysis.

GFX requires two continuous measurements to be made to fully isolate the species of interest. If we consider, e.g., the measurement of HCl, one of these measurements (the live channel) is made extremely sensitive to HCl by limiting the waveband of energy measured to such that is readily absorbed by HCl. This is achieved by using a narrow-band-pass-optical filter that only passes energy at 3.6 microns. Although this waveband of energy is very sensitive to HCl, other species may be present that also absorb energy in this band. A second (reference) channel is therefore necessary to measure the effect of these other interfering species. It is made specially insensitive to HCl by placing a sealed, non-consumable gas cell, containing 100% HCl in its optical path. This saturates the reference channel with HCl and leaves it sensitive only to the interfering species.

A viable alternative to GFX can be provided by DOAS (Dual Optical Absorbance Spectroscopy). However, limitations become apparent when isolating some species of interest from combustion processes. Many of these species are heavily masked by other major products of combustion. Accurate analysis in these circumstances requires the use of GFX.

Both alternative solutions, i.e., the upgrade of the existing multigas analyser by the

retrofit of HCl measurement channel and delivery of a new instrument allowing all required measurements including HCl, have been successfully proven in several Polish cement plants. Unfortunately, the method described is not useful for HF measurement because of its extremely low concentration (usually below 1 mg/m_n^3).

- 2. Analyser with diode laser [2]

Several spectroscopic techniques alternative to NDIR have been developed for measuring trace concentration of gas. One of the most successful is tuneable diode laser absorption spectroscopy (TDLAS) based on laser wavelength modulation. In order to minimise the influence of residual amplitude modulation (RAM) caused by laser wavelength modulation, harmonic components are selected for measurement. Practise has confirmed that the second harmonic signal assures negligible influence of RAM and acceptable signal amplitude.

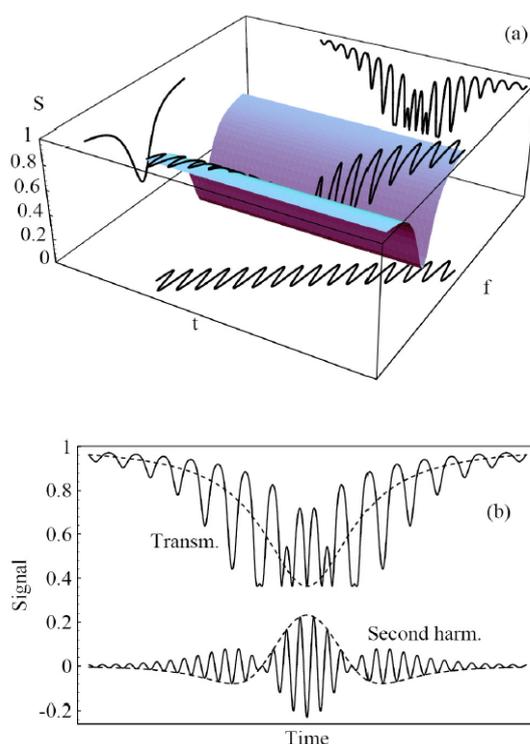


Fig. 1. Schematic drawing of a dual modulation technique

In up-to-date instruments, the dual modulation (ramp scanning) technique is applied. In addition to a high-frequency modulation, the laser centre frequency is scanned over the absorption line at low frequency. This is shown in figure 1a [2], where a normalised detector signal S is plotted as the function of the time (t) and an

instantaneous laser frequency (f). The shaded surface represents the absorption line. The detector signal is represented by the space curve embedded in the shaded surface. The projection of the curve onto the plane $t-s$ is the detector signal as a function of time being repeated in figure 1b. The envelope of the second-harmonic component of the signal is used for detection of the measured gas.

There is, however, a type of interference that may influence the concentration measured. This is the effect of absorption line broadening originating from molecular collisions, mostly with two species always present in flue gas, i.e., water vapour and carbon dioxide. Automatic compensation of the effects of line broadening can successfully be done by digital processing of absorption line scaleshape.

Diode laser analysers are used in CEM systems first of all to measure HF concentration (and HCl if necessary). TDLAS analysers are built to measure a single gas concentration whereas their accuracy allows the measurements below 1 mg/m_n^3 .

2.2. MEASUREMENTS OF THE CONCENTRATION OF TOTAL ORGANIC CARBON

Current regulations require the application of Flame Ionisation Detector (FID) technique whose measuring principle is based on the ionisation of hydrocarbons in hydrogen flame. The burning of hydrocarbons results in an ionisation current being dozens of times stronger than that created by pure hydrogen flame. Constant gas sample and hydrogen stream are drawn in the burner nozzle whose potential is negative. The mixture is burned by adding a hydrocarbon-free air.

FID does not differentiate between species since it responds to carbon-hydrogen bonds rather than to specific compounds. Generally, the response of a FID is mostly influenced by the number of carbon atoms in a sample. Furthermore, FIDs only respond to the molecules in gaseous or vapour phase. Table 2 [3] shows the relative responses of FIDs to organic compounds.

Table 2

Responsiveness of FIDs

Class of compound	Example	Sensitivity
Aromatics	benzene, toluene, xylene	excellent
Alkanes	butane	excellent
Alkenes/alkynes	ethane/ethyne	excellent
Ketones	MEK	good
Alcohols	butyl alcohol	good
Aldehydes	formaldehyde	poor
Chlorinated compounds	dichloromethane	very poor

The measuring principle and the above mentioned limitations put on the method sensitivity may cause that in some unfavourable circumstances (e.g., in the case of numerous compounds comprising chlorine) the instrument may display too low value and it is rather unusual that it shows too high value. It is particularly difficult to compare the FID readings with the results obtained using another method, e.g., wet analyse or chromatography. These methods enable us to determine the participation of particular compounds in a sample and one cannot be sure that all components have been taken in consideration. In such a case, FID reading is usually more realistic.

3. EXAMPLE OF APPLICATION OF CONTINUOUS EMISSION MONITORING SYSTEM IN A WASTE FUEL CO-COMBUSTION PLANT

Figure 2 shows the layout of CEM system built by Pentol in one of Polish cement plants. The set of instruments installed on each of two stacks strictly corresponds to the requirements given in the Appendix 6 to Regulation [1] mentioned in chapter 1 and the preferences described in chapter 2.

The system consists of:

- Optical “in situ” NDIR analyser measuring in GFX technique the concentration of the following gases: SO₂, NO_x, CO, CO₂, HCl and water vapour – G-CEM 4000 model manufactured by Codel International; an important advantage of the instrument is reliable measurement of water vapour which enables a precise compensation for cross-sensivities and conversion of all recordings to dry exhaust gas as required by law.

- Optical “in situ” diode laser analyser measuring HF concentration in near IR using TDLAS technique – LaserGas model manufactured by Norsk Elektro Optikk.

- FID analyser measuring Total Organic Carbon–Thermo-FID MK model, manufactured by M&A Analysentechnik GmbH; a chosen model consists of measuring head mounted directly on the stack – this makes the instrument compact and minimises the scope of maintenance.

- “In situ” zirconia oxygen analyser – model CAT-4 manufactured by TTM Elektronika.

- Optical dust monitor with twin transceiver heads mounted on the opposite sides of the stack – D-CEM 2000 model manufactured by Codel International.

- Optical flowmeter that measures in IR based on cross-correlation technique – V-CEM 5000 model manufactured by Codel International.

In the system, the use is made of digital data transmission, including remote diagnostic function. Software for data storage, processing and presentation, including emission report generation, meets all legislative requirements. The operation period of CEM systems allows a conclusion that they are characterized by the features guaranteed by manufacturer, first of all very low maintenance expenses.

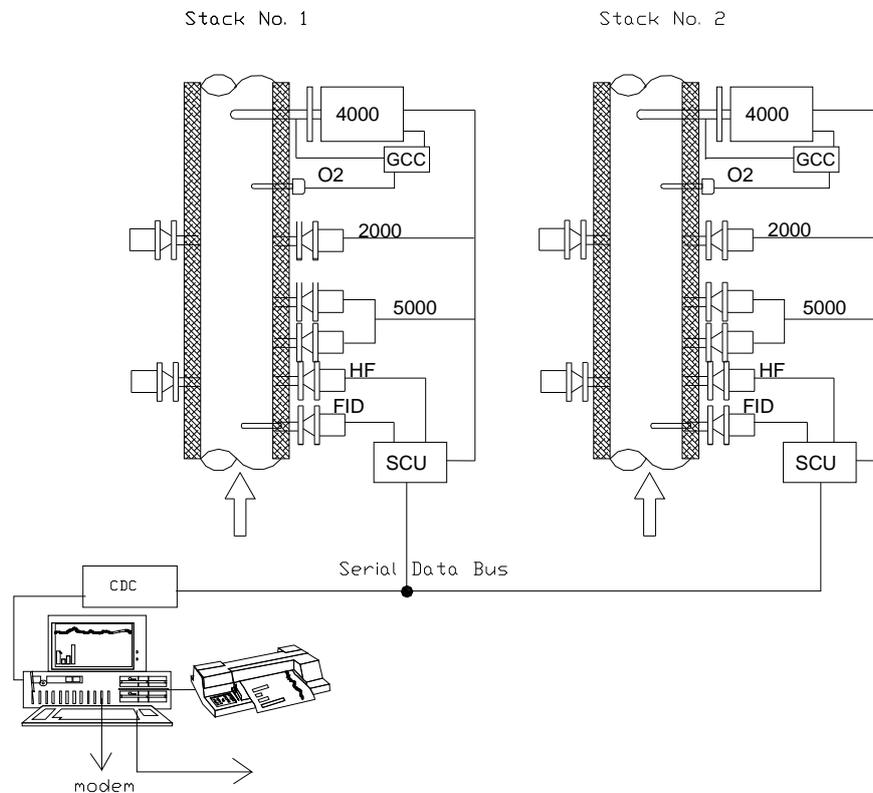


Fig. 2. The layout of CEM system for a cement plant:
 GCC – gas calibration controller, SCU – station control unit,
 CDC – central datapoint controller, other explanations in the text

LITERATURE

- [1] Regulation of the Minister of the Environment of 23rd December 2004 on requirements concerning the measurement of emission quantities.
- [2] LINNERTUD I., KASPERSEN P., JAEGER J., *Gas monitoring in the process industry using diode laser spectroscopy*, Applied Physics B, 1998, Vol. 67, 297–305.
- [3] Technical Guidance Note M16 (Monitoring). The measurement and monitoring of volatile organic compounds to air from industrial installation, Environmental Agency, 2005.

DOŚWIADCZENIA „PENTOLU” W ROZBUDOWIE SYSTEMÓW MONITORINGU EMISJI UMOŻLIWIAJĄCEJ POMIARY WYMAGANE PODCZAS SPALANIA ODPADÓW I PALIW ALTERNATYWNYCH

Przepisy precyzują zakres pomiarów ciągłych do celów monitoringu emisji w zależności od rodzaju spalanego paliwa. W porównaniu z instalacją energetycznego spalania paliw, spalanie bądź współspala-

nie odpadów wymaga dodatkowo ciągłego pomiaru stężenia chlorowodoru, fluorowodoru i całkowitego węgla organicznego. Przeanalizowano dostępne technicznie i dopuszczone przez przepisy metody pomiarów tych związków. Optymalne techniki pomiarowe różnią się od technik stosowanych do pomiarów podstawowych, co uniemożliwia (poza pomiarem HCl) rozbudowę istniejących analizatorów. Omówiono problem interpretacji uzyskanych wyników pomiarów całkowitego węgla organicznego. Opisano koncepcję pomiaru emisji zrealizowaną w ostatnich latach w trzech polskich cementowniach.